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CURRENT TRENDS IN EVAPORATOR FOULING

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ABSTRACT

A second IPST survey of evaporator fouling in the North American kraft pulping industry was conducted in 1997. The objective was to assess the nature and extent of these fouling problems, and the changes since the first survey conducted by Grace in 1974-75. A questionnaire and a request for black liquor and scale samples were distributed to 40 kraft pulp mills. This questionnaire requested detailed information on the nature of the wood supply, the pulping process and conditions; liquor processing; a description of the evaporator equipment configuration, performance characteristics, and scaling conditions of the evaporator system; and the liquor and scale composition. 25 mills returned a completed questionnaire, and 19 submitted liquor samples. The black liquor samples were analyzed for total solids content, total carbon, hydrogen, oxygen, sulfur, metals content, anions, residual active alkali, fiber, and residual soap content. The scale samples were analyzed for inorganic phase composition by X-ray diffraction.

The key results of the survey are that the average product solids content from evaporator trains is higher today, 58% versus 49%, a result of the current widespread use of falling film technology with liquor recirculation. More mills process hardwood liquors than in the 1970's. The black liquors processed contain more potassium, carbonate, and sulfate than they did in the 1970's, and probably more chloride. They contain the same amount of sodium, residual active alkali, and soap; and despite the impact of mill closure, the black liquors contain less of all other metals.

The average overall heat flux, average overall heat transfer coefficient, and average temperature difference per effect are down by 10%, 8%, and 3% respectively, compared to two decades ago. This is also the result of the increase in falling film concentrators that operate at lower heat fluxes and lower temperature differences. The frequency of soluble scales and of fiber, soap, organic scales have increased. Fewer mills report $CaCO_3$ scale problems, but fewer report no scale problems. Overall, the cleaning frequency is lower today than two decades ago. Boil-out frequency is down by 20%, and acid cleaning by 63%, but the frequency of hydroblasting is up by 130%.

INTRODUCTION

This project is the outgrowth of a workshop held at IPST in May, 1997 to discuss the state of evaporator fouling in the context of current operating conditions, changes in the characteristics of the feed black liquor due to pulping process changes, and throughput demands dictated by pulp production targets. The consensus among the attendees from the pulp and paper industry and evaporator manufacturers was that the severity of the problem has increased in recent years, and that there is a significant lack of scientific understanding of the inorganic chemistry involved when concentrating kraft black liquors to the high dry solids content (typically > 70%) that has become the current practice.

The workshop group identified an urgent need to generate experimental data on the solubility of various inorganic species, such as sodium carbonate, sodium sulfate, soluble calcium, and aluminosilicates, in black liquors concentrated to high solids. In addition, a parallel need was identified, and a plan of action was agreed upon, to survey the industry on the nature and extent of evaporator fouling problems and to identify the most influential variables.

This survey has five primary objectives: (1) to define the nature and extent of the fouling problem with hard data instead of with a collection of anecdotal experiential information, (2) to identify the most influential variables, both main factors and interactions, that can be correlated to liquor composition and evaporator operating parameters, (3) to compile a database of liquor chemical composition and evaporator operating and performance parameters so that normal or typical ranges for these variables can be established, (4) to evaluate the evaporator variables within the context of the overall mill and chemical recovery operations, and (5) to compare this survey's findings with those from a similar one conducted by Grace in 1974-75 [1].

BACKGROUND

Grace's Evaporator Fouling Survey

The fouling of black liquor evaporators is certainly not a recent phenomenon. A comprehensive survey of evaporator fouling problems was conducted by Grace [1] in conjunction with an experimental study of sodium sulfate and sodium carbonate solubility behavior in black liquors. He analyzed information obtained by questionnaire and by chemical analysis of the composition of liquor samples that were also submitted.

The major findings of his survey were that calculated values of the average heat fluxes for the evaporator sets of the reporting mills spanned a wide range, from 7,900 - 22,000 W/m^2 (2,500-6,900 Btu/ft^{2}hr). Similarly, the average overall heat transfer coefficients for these evaporator sets ranged from 720 - 1,870 W/m^{2}K (127-329 Btu/ft^{2}hr°F). These represent a nearly three-to-one range in the effective evaporative capacity per unit of evaporator surface area. Scaling appeared to be the primary factor responsible for this variability in productivity [1].

The most commonly reported scales were soluble (Na_2CO_3--Na_2SO_4) scales and calcium carbonate scales. Calcium carbonate scales appeared to constitute a more serious problem in the industry. In addition to being more difficult to remove, they had a dominant effect on evaporator productivity. Surprisingly, the data obtained in Grace's survey did not support the concept that rapid growing but easily removable soluble scales were responsible for most of the short-term degradation in evaporator performance while residual, insoluble calcium scales caused only a gradual deterioration in base-line performance. They indicate, instead, that substantial amounts of calcium scale can be removed by boiling out the evaporator with water, and that rapid growing calcium scales can govern the short-term performance [1].

The calcium content of the liquor was the most important variable affecting calcium scaling, and there are indications that the amount of calcium in the liquor was influenced more by wood supply than by internal process conditions. Parameters controlling the formation of soluble scale could not be identified, and no correlation could be established between scaling behavior and those variables associated with the solubility of Na_2CO_3 and Na_2SO_4 in black liquor. This was due, in part, to the dominance of calcium scales [1].

The data also suggested that some soap in the liquor is beneficial and that there may exist an optimum degree of soap removal. A beneficial effect of residual active alkali in the liquor was also indicated, but no correlation was established between the measured fiber content of the liquor and scaling [1].

Changes in Pulping and Evaporation Technology

In the early 1970's, almost all kraft pulping was by the conventional batch process, and evaporator configurations were almost exclusively of the long tube vertical (LTV) type with a rising liquor film flow pattern. These evaporators discharged the product liquor at approximately 50% dry solids content. To reach the firing solids of 60-65%, the liquor was then further concentrated in venturi cyclone or cascade type direct contact evaporators (DCE).

Since that time, several significant process changes have directly and indirectly impacted the operation and performance of evaporator sets. New pulping technologies were developed and commercialized in the 1980's: Kamyr's Modified Continuous Cooking (MCC®) and Extended Modified Continuous Cooking (EMCC®), Beloit's Rapid Displacement Heating (RDH®), and Sund's Defibrator's Superbatch® processes have become established as older units have been retrofitted and new capacity has been brought on line [2, 3]. These new processes have fundamentally changed some of the chemistry in the black liquor evaporator feed. For example, black liquor is contacted with fresh wood chips before heading toward the evaporators. This results in an increased calcium load in the liquor in the form of organically bound calcium which is thermally unstable and can decompose in the higher temperature effects, releasing free calcium which will combine with the abundant carbonate ions to form insoluble calcium carbonates.

Significant changes have also occurred to evaporator systems. New evaporator geometries have been commercialized to mitigate scaling problems, increase capacity, and raise the discharge solids content [4]. Two of these designs are tube type and dimple plate type falling film evaporators. Concurrently, there was a move toward low odor recovery boilers, and a drive to increase the dry solids content of the liquor fired to increase recovery boiler capacity and improve steam production. This resulted in replacement of many DCE's with various types of black liquor concentrators to raise the discharge solids from the usual ~50% exiting the multi-effect evaporator train to a dry solids content at firing of at least 65-70%, and in some cases as high as 80%.

Some of these concentrators are forced circulation type evaporators, which can either stand alone and receive 45-50% solids from an LTV train or be integrated as the final effect of a falling film set. Two commercialized units are the PFR® Concentrator by Unitech Corporation, and the High Solids Crystallizer by US Filter/HPD which is a forced circulation evaporator/crystallizer. Finally, additional units, so called "superconcentrators", have been added at a small number of mills to reach ~80% solids. These are falling film crystallizer/concentrators with high liquor recirculation rates and introduced seed crystals to promote sodium carbonate crystal growth in the bulk solution rather than on heating surfaces, or tube type falling film evaporators or crystallizer type concentrators operating at high temperatures and pressures. These units are followed by one or more flash tanks to incrementally gain additional evaporation [4].

Mill Closure

A further development has been mill closure, or the drive to reduce overall mill water consumption through recycling and multiple water uses. One adverse side effect of this effort has been the increase in the concentrations of non-process elements (NPE's) in the chemical recovery cycle. These are metal ions such as aluminum, barium, calcium, magnesium, manganese, and silicon, to name the more critical ones. To avoid precipitation of these compounds, in characteristically undesirable locations, effective purging of these elements is necessary in current operating practices. It would be interesting to compare the concentrations of these NPE's in today's black liquors with the results of Grace's study.

PROCEDURES

Survey

An updated evaporator fouling survey questionnaire was developed by Grace based on his original survey, and was distributed to individual mills at a number of North American pulp and paper companies. No attempt was made to blanket the entire industry with this questionnaire, but rather, selected companies were contacted based on their participation in the evaporator fouling workshop mentioned above. This original set of participants was later expanded as the authors interacted with additional mills, some of whom were not experiencing any serious scaling problems, but were eager to participate nonetheless. All told, approximately 40 mills were contacted.

The questionnaire targeted numerous aspects of the entire mill's operation, and a complete description of the design and operation of the evaporator and concentrator systems. The information requested included the nature of the wood supply, the type of pulping process and conditions, white liquor composition, mill water composition, black liquor processing operations such as oxidation and soap removal, a description of the evaporator set(s) and separate concentrator(s) (where appropriate), evaporator operating parameters under various conditions, types and frequencies of cleaning procedures, and types of reported scales and related scaling conditions. Black liquor samples from just upstream of the fouling effect and any available scale samples were also requested.

In order to perform energy balances around the evaporator sets, so that average heat fluxes and heat transfer coefficients could be calculated, additional follow up requests for information were made for data on boiling point rises in the individual effects, and various feed and product liquor and vapor temperatures.

Analytical Procedures

Black liquor samples were analyzed for total solids, and metals by acid digestion followed by Inductively Coupled Plasma (ICP) spectroscopy. Anions (chloride, sulfate, thiosulfate, and oxalate) were analyzed by Capillary Ion Electrophoresis (CIE). Total carbon, oxygen, hydrogen, and sulfur were determined from combustion analyses, carbonate was determined coulometrically by measuring the amount of evolved carbon dioxide from acidified samples, and total organic carbon was determined as the difference between total carbon and total inorganic (carbonate) carbon. Residual active alkali (RAA) was measured by acid titration after precipitation of the inorganic matter and carbonate with barium chloride. The fiber content of the liquor was measured by filtration, and the residual soap content by organic solvent extraction. The scale samples were analyzed for inorganic phase composition by X-Ray Diffraction (XRD).

Data Reduction

The data was entered into a Microsoft Access database. To estimate the evaporator performance, an energy balance calculation was performed for every evaporator set where sufficient data were available. Average values for the operating heat transfer coefficients, thermal driving forces, and heat loads were calculated, accounting for both sensible and latent heat changes in the liquor.

When actual data from the mill were not provided, the sum of the boiling point rises (BPR) was estimated by assuming equal masses of water were evaporated in each evaporator body, calculating the corresponding solids contents, and estimating the BPR from an established BPR solids correlation [5]. For evaporator effects with more than one body, the BPR for the effect was taken as the mean BPR for the respective bodies. Comparing actual BPR data with BPR's estimated as described above, the sum of the estimated BPR's is generally within 20% of the actual sum of the BPR's. Also, the corresponding average temperature difference per effect, and the average heat transfer coefficient per effect, based on the estimated BPR's, are within 10% of those values calculated using actual BPR data.

Statistical Analysis of Data

A statistical analysis of the data will be performed for the final version of this paper. This will consist of analysis of variance calculations between pairs of variables to determine if any correlation exists between evaporator operating variables, black liquor composition variables, and the types and extent of reported scaling.

RESULTS AND DISCUSSION

Distribution of Survey Responses

The overall status of the responses to the questionnaire and the geographical distribution of those responses based on mill location and wood supply are presented in Table I. To date, of the 40 mills contacted, 27 have responded: 25 returned a completed questionnaire, 17 of those also submitted liquor samples, and two mills submitted only a liquor sample for analysis.

The distributions of the respondent mills based on type of pulping process employed, geographic location, and nature of the wood supply, highlight some expected trends, and some important differences from Grace's survey. A small, but significant number of mills use a modified kraft cooking process: MCC®, EMCC®, RDH®, or Superbatch®. These processes can alter the traditional chemistry of the weak black liquor fed to the evaporators. Although these processes still represent a minority of the respondents, their installed capacity will likely increase as old units are retrofitted and new ones are installed. In Grace's survey, none of the mills used a modified kraft process, they were all either conventional kraft, soda, NSSC, or kraft + semi-chemical mills [1].

The geographic distribution of the respondents has been weighted towards the Southeast and Northwest regions. This is an unintended consequence, and may indicate regions where fouling is more prevalent. As may be expected, the nature of the wood supply varies substantially in different regions of the USA and Canada. In the Southeast, two of the ten mills pulp a majority of hardwood, and the remaining eight are majority softwood mills with two pulping 100% softwood. This is more the expected pattern for southeastern mills. The three mid-south mills pulp a majority of hardwood, but less than 80%. In the Northeast, all three mills pulp a majority of hardwood with two pulping 100% hardwood. The lone central mill, and the two north central mills pulp 85-95% hardwood. Finally, in the Northwest, all the mills pulp at least 67% softwood, and three pulp 100% softwood. Overall, for the 25 mills completing the questionnaire, the mean values for softwood, and hardwood production are 55.4%, and 44.6%, respectively. This is substantially different from Grace's survey, where the mean level of hardwood production was 31%.

Table I. Survey responses and geographical distribution of respondents

Pulping Processes Employed	Completed Questionnaires	Liquor Samples[a]	Scale Samples[b]	Wood Supply[c] HW>80%, SW>80%
Conventional Kraft	18	13	4	4, 4
Modified Kraft[d]	5	5	3	1, 2
Kraft + NSSC/Green Liquor[e] (cross recovery)	2	1	1	0, 0
Geographic Region				
Southeast (AL, FL, GA, MS, NC, SC,VA)	10	9	4	0, 2
Midsouth (AR, LA, OK, TX)	3	1		0, 0
Northeast (DE, MD, Mid-Atlantic, New England)	3	2		2, 0
Central (IL, KY, OH, WV)	1	2	2	1, 0
North central (MI, MN, WI)	2	2	2	2, 0
Northwest (ID, OR, WA; Canada: AB, BC)	6	3		0, 4
Total responses	25	19	8	5, 6

[a] The number of mills that submitted black liquor samples. Some mills submitted multiple samples: for multiple evaporator sets and/or multiple samples from one set.
[b] The number of mills that submitted scale samples. Several mills submitted multiple scale samples representing different types of scale.
[c] The number of mills with a wood supply that is, on average, > 80% hardwood, and > 80% softwood.
[d] Modified kraft processes include MCC®, EMCC®, RDH®, and Superbatch®.
[e] NSSC/Green Liquor pulping accounts for 15%, and 33%, respectively, of total pulp production for the two mills reporting. One of the mills employs kraft EMCC® pulping.

Evaporator System Geometries

Most of the mills that participated in this survey have more than one evaporator set: the 25 mills that returned the completed questionnaire operate a total of 49 evaporators, and 25 separate stand alone concentrators. These evaporators and concentrators represent a variety of different types and geometries: LTV rising film, tube type and plate type falling film, blow heat falling film (2 sets), tube type falling film high pressure evaporator, falling film crystallizer/concentrator, and forced circulation evaporator/crystallizers. This is a marked change from Grace's survey of the 1970's when all the evaporators were of the LTV rising film type, although several did have falling film, or forced circulation first effects. Since that time, many mills have integrated one or two falling film concentrator bodies as a new first effect into their existing LTV evaporators, have installed newer tube type or plate type falling film evaporators where the first effect concentrates the liquor to 65-68%, and/or installed additional stand alone high solids concentrator units of the type mentioned above. However, from the information provided by the mills, the true number of evaporator effects and bodies, and the arrangement of liquor and vapor flows, was not always clear. The mill's effect/body numbering scheme was often inconsistent with the diagrams.

Types and Location of Reported Scale

The distribution of the types of reported scale is presented in Table II, and is a composite of data reported by the mills and compositional analyses of the submitted scale samples. The distribution of the scaling locations based on the approximate liquor solids range is presented in Table III. As one would expect, most mills experiencing scaling reported more than one type of scale.

Table II. Types of scale reported

Type of Scale	Number of Mills Reporting (%)	
	This Survey	Grace's Survey
Burkeite (soluble) scale, Na_2CO_3—Na_2SO_4	17 (35%)	19 (28%)
Calcium carbonate	11 (22%)	20 (30%)
Fiber, soap, and/or other organics	9 (18%)	6 (9%)
Aluminosilicates, and other silicates	4 (8%)	9 (13%)
Pirssonite, $Na_2CO_3.CaCO_3$	1 (2%)	
Sodium oxalate, $Na_2C_2O_4$	1 (2%)	
Other inorganic scale[a]	1 (2%)	
No scale	2 (4%)	10 (15%)
No information	3 (6%)	3 (4%)
Total	49	67

[a] From XRD analysis, the scale sample from this one mill consisted of burkeite, erdite ($NaFeS_2.2H_2O$), and magnetite (α-Fe_3O_4).

Table III. Location of reported scaling

Scaling Location	Liquor Solids Range, %	No. of Mills Reporting
Evaporator Effects Traditional effects excluding integrated concentrator units.	< 30	3
	31 - 40	3
	41 - 50	10
	51 - 60	7
Concentrator Effects Separate unit or integrated 1st effect of evaporator train.	51 - 60	5
	61- 70	10
	71 - 80	2
Total		40

Since the critical solids concentration for burkeite precipitation is generally between 47 and 53% dry solids content, the high percentage of mills reporting scaling in the 41-50% and 51-60% ranges in their traditional evaporator effects and concentrator effects is generally burkeite.

In climbing film LTV evaporators, scaling most frequently occurs in the tubes and liquor distributor plates. Because boiling takes place in the bulk liquor phase as it rises in the tubes, dry spots can develop on the tube walls and provide locations for scale formation. In fact, where mills have reported the data, scaling has primarily occurred in these locations. This points out an inherent design limitation of climbing film LTV evaporators compared to falling film units. Scaling is less of a problem in falling film units, but tube pluggage can still occur, and is usually caused by poor liquor distribution. In plate type falling film units, pluggage cannot occur. Falling film units are also run at lower steam pressures than LTV systems which minimizes the scaling caused by reverse solubility compounds such as Na_2SO_4, or temperature sensitive calcium complexes [4]. In forced circulation units, if the recirculation rate is not high enough, or the liquor inventory is too low, scales can form in the heat exchanger tubes, or the surfaces of the vapor bodies.

The accepted operating procedure is to run climbing film LTV evaporator effects to produce liquor 1-2% below the critical solids level at which burkeite begins to precipitate, and to run the concentrator effects above this level. For falling film units that are designed for precipitation of sodium salts in suspension, crossing the critical solids level for burkeite precipitation does not require a change in evaporation technology.

Evaporator Performance Parameters

A summary of evaporator performance parameters from this survey, and Grace's survey, are presented in Table IV. The average values for the heat flux, temperature difference per effect (ΔT), heat transfer coefficient, and steam economy, are based on heat balances for only five evaporator systems. A more complete set of data will be presented later. The available results show some interesting trends:

1. Overall, cleaning frequency is lower today than two decades ago. Boil-out frequency is down 20% and acid cleaning by 63%. This suggests a better management of scale deposition in the evaporators. Hydroblasting frequency is up by 130%, however. The increase in hydroblasting frequency suggests that the frequency of more difficult to remove scales--$CaCO_3$ and aluminosilicates--would have increased. This does not agree with the results in Table II. The discrepancy may be due to the small number of scale samples obtained in this study.

2. The average product solids content from evaporator trains is higher today, 57.8% versus 48.6%. This is undoubtedly a result of the widespread use of falling film technology with liquor recirculation. Falling film units can operate above the critical solids content of black liquor (typically 47-53% dry solids content) without experiencing fouling problems.

3. The average overall heat flux, average overall heat transfer coefficient, and average ΔT are down by 10%, 8%, and 3% respectively, compared to two decades ago. This is also the result of the increase in falling film concentrators that operate at lower heat fluxes and lower ΔT's.

Table IV. Averages of evaporator performance parameters

	This Survey			Grace Survey (1974-75)		
Performance Parameter	**Mean**	**Std. Dev.**	**Range**	**Mean**	**Std. Dev.**	**Range**
Boil out frequency, times/mo.	3.25	3.24	.083-12.2	4.09	3.5	0.33 - 15
Acid cleaning freq., times/mo.	0.092	0.049	.042-.167	0.25	0.67	0 - 3.5
Hydroblasting freq., times/mo.	0.107	0.083	.056-.167	0.047	0.059	0 - 0.21
Total cleaning freq., times/mo.	3.16	3.80	.083-12.3	4.39		
Prod. Loss between cleanings, %				15.8	8.6	2.7 - 30.9
Rate of production decline, %/mo.				71.6	55.6	8 - 241
Evaporator product solids, wt. %	57.8	9.9	47 - 80	48.6	3.7	42 - 62
Average heat flux, W/m^2	13,100	2,520	9,810 - 16,000	14,500	3,130	7,880 - 21,800
Average ΔT, °C	12.4	2.2	10.6-15.9	12.8	2.8	9.3 - 23.3
Ave. heat transfer coef., W/m^2K	1,050	89	921-1,130	1,140	295	721-1,870
Saturated steam temp., °C	144	10	129 - 192	141	7.2	127 - 162
Steam economy	5.30	1.78	3.94-7.89			

Cleaning frequencies are generally not a very good measure of the degree of scaling because mills with no, or only minor scaling problems, will often boil out the evaporators once a year prior to vessel inspections. Similarly, boil-outs are often performed on a regularly scheduled basis even if there is insufficient performance loss due to scaling to warrant cleaning. They are used proactively as routine preventative measures to forestall significant performance declines, and not always reactively, to respond to obvious scaling problems.

The cleaning frequencies do not include data for evaporator sets where one body of a multi-body first effect is always in wash mode--this is more of a preventative measure and the data would seriously skew the overall averages. The total cleaning frequency is the sum of the boil-out, acid cleaning, and hydroblasting frequencies, and any other identified cleaning method, such as flushing the effects with warm water or hot condensate. Cleaning frequencies for both surveys are comparable, although the current survey shows lower boil-out and acid cleaning frequencies, and higher hydroblasting frequencies than Grace's survey as discussed above. As one would expect for this type of data, the ranges of values are quite large.

The evaporator product solids content data includes values for traditional evaporators, separate concentrators, and integrated evaporator/concentrators as discussed previously. Most mills also reported the product solids of the liquor exiting the flash tank as compared to exiting the last effect or concentrator. In general, a solids gain of one to two percent can be assumed for the flash tank. In Grace's survey, the reported solids values were for the liquor prior to the flash tank.

The average overall heat flux and the average overall heat transfer coefficient provide an estimate of evaporation capacity when comparing two evaporator trains. They are less useful for troubleshooting, however. Ideally, monitoring the average heat transfer coefficient for each effect as a function of time would be the best way to track the evaporator performance. However, this data was not requested because it was believed to be too difficult to obtain from the mills.

Black Liquor Composition

A summary of the black liquor composition data for the two surveys is presented in Table V. From a comparison of the analytical data, it is apparent that the mean composition of black liquor has changed since the 1970's, in some cases dramatically. Most notably, the Na_2CO_3 and Na_2SO_4 concentrations are both higher now; Na_2CO_3 by 15%, and Na_2SO_4 by 88%.

The sharp increase in sulfate concentration is probably due to the addition of R8 or R10 chlorine dioxide generator effluent rich in saltcake to various points in the liquor system. A number of mills reported adding it to the weak black liquor, and a few to the concentrator feed. In addition, a few mills reported adding tall oil acidulation waste to the weak black liquor, and one liquor sample was analyzed for a mill practicing cross recovery of kraft and NSSC black liquors, although NSSC production accounted for only 15% of total pulp production. The modest increase in carbonate concentration is more problematic and may simply reflect a causticizing conversion that is slightly lower now, and/or an analytical artifact that all of the carbonate was assumed to be sodium carbonate. The increase in potassium concentration noted in Table V may be in the form of potassium carbonate which would account for most of the increase in carbonate.

The black liquors submitted for analysis were also sampled at various locations. Most were first effect or concentrator feed samples, where the scaling primarily occurring, but a number of samples were weak or intermediate liquors. Several mills also sent multiple samples representing different evaporator sets and/or multiple samples from the same set.

The residual active alkali ($NaOH + Na_2S$), total sodium, and residual soap, are all comparable to the earlier set of data. The calculated critical solids is also essentially unchanged from the 1970's. This is somewhat surprising given that the Na_2CO_3 and Na_2SO_4 concentrations are both significantly higher now. However, the critical solids calculation is much more sensitive to the total sodium concentration, and that value has not changed appreciably. The potassium level is now 49% higher which is probably an effect of mill closure. The fiber content is almost an order of magnitude greater, probably because a smaller pore size filtering medium was used: ~30 μm pore size instead of the ~60 μm for the previous study.

The trace metals (NPE's), with the exception of calcium, are all significantly lower. This is somewhat surprising considering the expected effects of mill closure on the recovery cycle are to increase concentrations of these elements, but it does indicate that there is adequate purging of these compounds, probably during green liquor clarification.

Table V. Averages of black liquor composition variables

Analyte	This Survey			Grace's Survey (1974-75)		
	Mean	Std. Dev.	Range	Mean	Std. Dev.	Range
Na_2CO_3, wt. %	10.0	2.6	4.77 - 14.5	8.7	1.45	6.6 - 12.3
Na_2SO_4, wt. %	6.03	4.18	1.94 - 16.1	3.2	1.5	0.9 - 8.3
Na_2CO_3/ Na_2SO_4	2.49	1.67	0.51 - 6.33			
Na_2S, wt. %	0.79	0.92	0.06 - 2.97			
Residual active alkali as Na_2O, wt. %	5.69	1.36	2.81 - 7.66	5.95	1.05	3.9 - 8.6
Sodium, wt. %	18.4	1.65	14.0 - 20.3	18.7	0.88	17.2 - 20.5
Potassium, wt. %	2.02	1.19	0.82 - 5.05	1.36	0.57	0.44 - 2.7
Residual soap, wt. %	0.85	0.48	0.32 - 2.02	0.93	0.42	0.32 - 1.62
Fiber[a], wt. %	0.23	0.24	0.04 - 1.08	0.031	0.031	0.001 - 0.159
Critical solids, wt. %	52.2	2.8	49.0 - 60.3	52.9	2.1	48.4 - 56.3
Carbon, wt. %	34.6	2.32	31.4 - 40.4			
Inorganic carbon, wt. %	1.14	0.30	0.54 - 1.64			
Organic carbon, wt. %	33.5	2.50	30.2 - 39.7			
Hydrogen, wt. %	3.43	0.23	3.05 - 3.96			
Oxygen, wt. %	35.1	2.57	26.4 - 38.4			
Sulfur, wt. %	4.74	0.89	3.34 - 6.65			
Sulfate, wt. %	4.08	2.83	1.31 - 10.9			
Thiosulfate, wt. %	3.98	1.25	2.40 - 6.49			
Chloride, mg/kg	4,810	3,170	1570-12,700			
Oxalate, mg/kg	5,250	3,350	2000-13,400			
Aluminum, mg/kg	49.9	14.8	27.6 - 98.2	139	75	32 - 300
Barium, mg/kg	8.11	5.50	0.94 - 20.2			
Boron, mg/kg	42.0	21.9	24.4 - 132	202	153	49 - 680
Calcium[b], mg/kg	409	278	118 - 1,050	360 450	250 270	90 - 1,080 40 - 1,300
Copper, mg/kg	1.99	1.89	0.72 - 10.2	77	116	7 - 510
Iron, mg/kg	28.9	7.6	18.3 - 49.2	91	16	56 - 120
Magnesium, mg/kg	167	83	29.3 - 309	184	30	140 - 240
Manganese, mg/kg	55.1	24.4	15.1 - 93.1	96	37	42 - 220
Phosphorus, mg/kg	85.0	20.9	53 - 118			
Silicon, mg/kg	676	345	367 - 2,080	1,140	400	240 - 1,800
Strontium, mg/kg	2.93	2.27	0.65 - 8.6			
Vanadium, mg/kg	43.4	50.4	1.39 - 166	111	141	7 - 600
Zinc, mg/kg	8.46	3.91	3.55 - 19.4			

[a] Fiber measurements differed in the pore size of the filters used.

[b] In Grace's survey, two independent calcium determinations were made: by atomic absorption spectroscopy (first entry), and by atomic emission spectroscopy (second entry).

Overall Mill and Chemical Recovery Operations

It is important to examine evaporator performance in the context of the overall mill and chemical recovery operations because performance problems rarely originate in the evaporator systems themselves, they are almost always "inherited" from somewhere else. The white liquor composition data that is presented in Table VI is mill reported data, and is a valuable barometer for the effectiveness of two important chemical recovery processes. One is causticization of the green liquor to white liquor, as measured by the causticizing efficiency (CE). The other is reduction of the sulfate to sulfide in the recovery boiler, as measured by the reduction efficiency (RE). Causticization and reduction are two important processes that directly affect the burkeite scaling tendencies of the liquor because they determine the residual sodium carbonate, and sodium sulfate, respectively, that are carried through the liquor system as a dead load.

Table VI. Averages of white liquor composition variables

Parameter	This Survey			Grace Survey (1974-75)		
	Mean	**Std. Dev.**	**Range**	**Mean**	**Std. Dev.**	**Range**
Tot. Titr. Alkali, as Na_2O g/L	119	7.0	102 - 139			
Active Alkali, as Na_2O g/L	99.2	6.9	85.7 - 119	110.6	43.6	83 - 180
Causticizing Efficiency, %	79.1	3.4	68.0 - 84.0			
Reduction Efficiency, %	92.9	3.1	83.0 - 97.9			
Na_2S, g/L	35.4	5.4	26.4 - 43.3	34.1	11.7	0.3 - 80
Na_2CO_3, g/L	34.1	7.8	23.6 - 52.1	29.6	12.5	1.0 - 49.4
Na_2SO_4, g/L	4.8	2.0	1.1 - 9.9	8.0	6.9	0.1 - 30

The CE values reported by the mills were probably determined directly from the measured white liquor composition without correcting for the NaOH content of the original green liquor. They are therefore slightly higher than the true values obtained if the correction for NaOH in the green liquor is accounted for. Similarly, the RE values were probably reported as sulfide/(sulfide + sulfate), instead of as sulfide/total sulfur, and were probably determined directly from the measured green liquor composition instead of from an analysis of the smelt composition. The mills generally did not specify the basis for the measurements. An exception may be one that was reported as 97.9%.

The causticizing efficiency and sulfur reduction efficiency reported by the mills should be maintained as high as possible subject to chemical equilibrium limitations to minimize the concentrations of sodium carbonate and sodium sulfate, respectively. In Table VI, the mean values for the CE and RE of 79% and 93% are good, but the relatively wide range of values underscores that some mills are operating with a poor CE and/or RE. In fact, one mill had a CE of 68% and a RE of 94%! The corresponding black liquor composition was 14.47 % Na_2CO_3, and 2.97% Na_2SO_4, for a ratio of Na_2CO_3/Na_2SO_4 of 4.87.

Comparing the data for the two surveys, we find that today's white liquors have concentrations of active alkali, and Na_2SO_4, that are 10%, and 40% lower, respectively, than in the 1970's and have a much smaller range of values. The reduction in sulfate concentration is opposite to the black liquor composition. This may due to adequate reduction of the higher sulfate load in the black liquor. The Na_2S concentrations are approximately the same, but the range of values is smaller in today's white liquors. The Na_2CO_3 concentration is 15% higher now which is the same increase in concentration that was reported for the black liquors. As was discussed previously, this increase in Na_2CO_3 concentration may reflect a slightly lower causticizing conversion, and/or an artifact of the analysis. The ranges of reported values in Grace's survey are especially astonishing. This may be partially due to the fact that his survey included data for seven kraft + semi-chemical mills practicing cross recovery, and two soda mills, in addition to the 37 kraft mills.

CONCLUSIONS

This survey of evaporator fouling in the North American kraft pulping industry has identified both similarities and differences in the nature and extent of the problem since Grace's survey in the 1970's. These characteristics are a reflection of the changes in pulping technology and evaporation technology, and changes in mill wide processes such as mill closure, and are manifested in the types and distribution of scales, evaporator performance parameters, and the composition of the processed black liquors.

The key results of the survey are that the average product solids content from evaporator trains is higher today, 58% versus 49%, a result of the current widespread use of falling film technology with liquor recirculation, and the fact that a number of evaporator sets now have integrated concentrators. More mills process hardwood liquors than in the 1970's. The black liquors processed contain more potassium, carbonate, and sulfate than they did in the 1970's, and probably more chloride. They contain the same amount of sodium, residual active alkali, and soap; and despite the impact of mill closure, the black liquors contain less of all other metals.

The average overall heat flux, average overall heat transfer coefficient, and average temperature difference per effect are down by 10%, 8%, and 3% respectively, compared to two decades ago. This is also the result of the increase in falling film concentrators that operate at lower heat fluxes and lower temperature differences. The frequency of soluble scales and of fiber, soap, organic scales have increased. Fewer mills report $CaCO_3$ scale problems, but fewer report no scale problems. Overall, the cleaning frequency is lower today than two decades ago. Boil-out frequency is down by 20%, and acid cleaning by 63%, but the frequency of hydroblasting is up by 130%.

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